## Idaho State Department of Agriculture Division of Agricultural Resources



# Quarterly Monitoring for Pesticides in Ground Water in Owyhee, Payette, and Washington Counties, Idaho 2009 - 2010



ISDA Technical Summary #44

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#### Introduction

In 2009, the Idaho State Department of Agriculture (ISDA) Ground Water Program was awarded a grant by the Environmental Protection Agency (EPA) to test ground water for currently registered pesticides. The goal of the project was to conduct quarterly monitoring of ground water for pesticides in areas where there have been frequent and elevated detections. The grant provided resources to conduct testing of pesticides at privately owned domestic wells in southwest Idaho (Figure 1). The testing was undertaken to develop a better understanding of impacts from registered active ingredients that have been detected in Owyhee, Payette, and Washington Counties. Laboratory results indicated that there are pesticide detections that are of concern and should be evaluated and tracked over time. Some detections were near specific pesticide health standards for drinking water. ISDA is working to implement the Idaho Pesticide Management Plan (PMP) and associated rules to protect ground water. ISDA is working to educate applicators and land owners on these issues.

# **Background**

The ISDA Division of Agricultural Resources is responsible for a variety of programs, laws, and rules for protection of ground water from pesticides. ISDA has a cooperative agreement with EPA to implement the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Staff implement the Idaho Pesticide Laws and Rules and conduct monitoring duties to fulfill this cooperative agreement. Additionally, the Idaho PMP, and the Rules Governing Pesticide Management Plans For Ground Water Protection (IDAPA 02.03.01) (Idaho PMP Rule) require the state to respond to pesticide detections in Idaho ground water. The state response as outlined in these two documents is based on four distinct levels established by pesticide detection concentrations as they relate to a percentage of a reference point. A reference point is based on a health standard, such as a maximum contaminant level (MCL), lifetime health advisory level (HAL), or reference dose (RfD). ISDA response actions increase and become more comprehensive as the detection level increases. The PMP

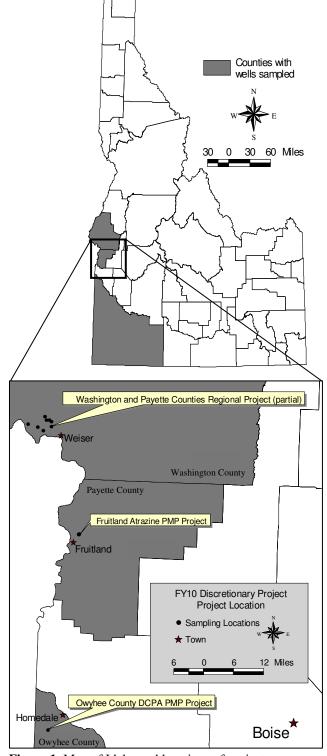


Figure 1. Map of Idaho and locations of project.

Rule divides the pesticide detections into the following levels:

**Level 1**: Detection above the laboratory detection limit to less than 20% of the reference point.

**Level 2**: Detection at 20% to less than 50% of the reference point.

**Level 3**: Detection at 50% to less than 100% of the reference point.

**Level 4**: Detection at or greater than 100% of the reference point.

#### **Historical Monitoring**

Since the 1990s, the ISDA Ground Water Program has conducted pesticide testing through local and regional-scale ground water monitoring in agricultural areas around the state. ISDA expanded pesticide sampling to include quarterly monitoring in areas that require additional response as the Idaho PMP Rule was implemented.

The goal of this project is to provide the ISDA Water Program with quarterly ground water monitoring data for three project areas where pesticides have been previously detected. The information will be used to make regulatory and/or voluntary changes related to applications of pesticides. ISDA will also conduct education relative to this project with landowners and pesticide applicators. The information can also be used for educational purposes and to advance technical knowledge relative to ground water quality protection and the application of Best Management Practices (BMP)

The objective is to prevent future ground water contamination and protect human health. Tasks to be conducted to meet these objectives are:

- Collect ground water samples from approximately 15 domestic wells for analysis of pesticides.
- Notify homeowners of their well testing results.
- Prepare data summary sheets at the completion of each sampling event and a technical report at the completion of all sampling summarizing significant findings.
- Meet with PMP Advisory Committee to determine what regulatory and/or voluntary practice changes will be recommended.
- Educate homeowners and pesticide applicators within the project area on findings and recommendations from PMP Advisory Committees.

#### **Pesticides Tested**

The samples collected were tested for 85 pesticides at the University of Idaho Analytical Sciences Laboratory (UIASL). ISDA has worked with the UIASL to create a specialized list of analytes that are registered for use in Idaho and have potential to reach ground water.

## **Description of Project Area**

The project includes aquifers within several southern Idaho counties including Washington, Payette, and Owyhee (Figure 1). The study area is located in several portions of the western Snake River Plain (Figure 1). The general aquifer type for each area is alluvial in nature.

## Washington County Quarterly Monitoring Area

The project area lies within the western Snake River Plain, a basin filled with sedimentary and volcanic rocks. The sedimentary rocks make up the major portion of the shallow aquifer in the project area. The shallow aquifer is composed of unconsolidated to poorly consolidated clay, silt, sand, volcanic ash, diatomite, freshwater limestone and conglomerates mostly deposited in a fluvial environment (Newton, 1991). A thick layer of blue clay underlies the shallow aquifer in the project area, which separates the shallow alluvial aquifer from the deeper sedimentary aquifer (Newton, 1991).

#### Payette County Quarterly Monitoring Area

The project area overlies an aquifer system limited to the Payette River Valley composed of unconsolidated sands and gravels. There are two sources of ground water in the project area, a shallow unconfined alluvial aquifer and a deeper blue clay aquifer. Wells chosen for this project are completed in the shallow unconfined aquifer. All project wells are completed in unconsolidated sands and gravels. Locally, shallow ground water flow is likely to the north towards the Payette River.

#### Northern Owyhee County Regional Project Area

The sediments in the project area are classified as the Idaho Group geologic formation (U.S. Geological Society, 2000). The sediments are believed to be deposited by prehistoric Lake Idaho and recent deposition from the Snake River. A "blue clay" layer is reported in well drillers' reports on file at IDWR for many of the project wells. The blue clay layer is part of the Glenns Ferry Formation and the low permeability of the clay produces a confined aquifer under the layer (Othberg, 1994). Ground water used for domestic purposes in the project area appears to come from two

sources: (1) a shallow system of coarse grained sands and gravels, and (2) a deeper confined system of black sand under the blue clay layer (Carlson et al., 2001). Well drillers' reports indicate the shallow aquifer to be approximately 50 feet below the ground surface and the deeper aquifer to be located at varying depths, generally 300 feet or deeper. The shallow aquifer is composed of alluvial deposits, mainly sand and gravel, with a few thin interbedded clay layers. The general ground water movement appears to be toward the Snake River, which is an area of probable ground water discharge (Carlson et al., 2001).

#### **Methods**

Well sites for ground water pesticide testing were selected based on recent and historical pesticide data and detections. Each area was choosen for further study due to the presence of multiple and/or elevated pesticide detections. Determining pesticide trends for these areas is important for assessing the extent of the contamination to assist with the PMP implementation.

All sample collections followed established ISDA ground water monitoring standard operating procedures for sampling, handling, storage, and shipping. Samples were sent to the UIASL in Moscow, Idaho for analysis. UIASL used liquid chromatography/mass spectrometry analysis for pesticides utilizing modified EPA Methods. Duplicates, blanks, and matrix spikes/matrix spike duplicates were collected and submitted as a part of the quality assurance project plan.

#### **Results**

ISDA sampled a total of 15 wells with previous pesticide detections for 85 pesticides in the fall of 2009 and summer of 2010. Numerous detections occurred, including detections of pesticides that were previously tested for and commonly detected in Idaho's ground water. The pesticides positively detected in the first three quarters of sample collection included 2,4-DCBA, atrazine, bentazon, bromacil, chloromethane, deisopropyl atrazine, desethyl atrazine, DCPA (dacthal), dinoseb, metribuzin, simazine, tebuthiuron, and tetrahydrofuran (Tables 1, 2, & 3). All detections were below any health based reference point (Tables 1, 2, & 3).

Sampling results indicate some pesticide impacts have occurred to the shallow aquifers within each area sampled. Results are summarized and presented in the following sections.

#### **Washington County Detections**

Eleven different pesticides were detected west of Weiser

in Washington County during the first three quarterly monitoring events. The 11 pesticides detected, in order of the number of detections, include: desethyl atrazine (16), atrazine (10), bromacil (6), 2,4-DCBA (3), tebuthiuron (3), DCPA (dacthal) (2), deisopropyl atrazine (1), metribuzin (1), dinoseb (1), chloromethane (1), and bentazon (1) (Table 1). Atrazine and desethyl atrazine were often found in the same well during the same sampling period. One well had numerous pesticides detected during each sampling event, including seven different pesticides in November 2009, and four pesticides in May 2010 (Figure 2). The outdoor faucet was shut off during the February 2010 sampling event and a sample was not collected. Most wells with positive detections had more than one pesticide detected above the laboratory detection limit. All detections, except one, was within the Level 1 category established by the Idaho PMP Rule and below any Idaho or EPA health standards (Table 1 and Figure 2). The exception to this is the November 2009 testing from well 7100901 where desethyl atrazine was found at 2.00 µg/L, which was a Level 3 detection. The total November 2009 concentrations of atrazine and the breakdown products in the well was 2.41 µg/L. This was a combined Level 3 detection with desethyl atrazine at 2.00 µg/L, atrazine at 0.37 µg/L, and deisopropyl atrazine at 0.04 µg/L. The May 2010 desethyl atrazine detection was a Level 1 detection of 0.17 µg/L.

#### Payette County Quarterly Monitoring Area

Five different pesticides were detected in Owyhee County, southwest of Homedale, during the first three rounds of the quarterly monitoring events. The five pesticides detected, in order of the number of detections include: atrazine (9), desethyl atrazine (9), deisopropyl atrazine (8), bromacil (1), 2,4-DCBA (1) (Table 2). All three wells sampled had pesticide detections. All wells with positive detections had more than one pesticide detected above the laboratory detection limit. All of the pesticide detections during the first three quarters were at the Level 1 category as established by the Idaho PMP Rule and below any Idaho or EPA health standards (Table 2 and Figure 3). The total concentrations of atrazine and the breakdown products in one well was over the Level 2 category for all three quarters (Table 2). Time series plots for atrazine (Figure 5) and desethyl atrazine (Figure 6) indicate that the pesticides concentrations appear stable or have decreased slightly through the quarterly testing period.

#### Northern Owyhee County Regional Project Area

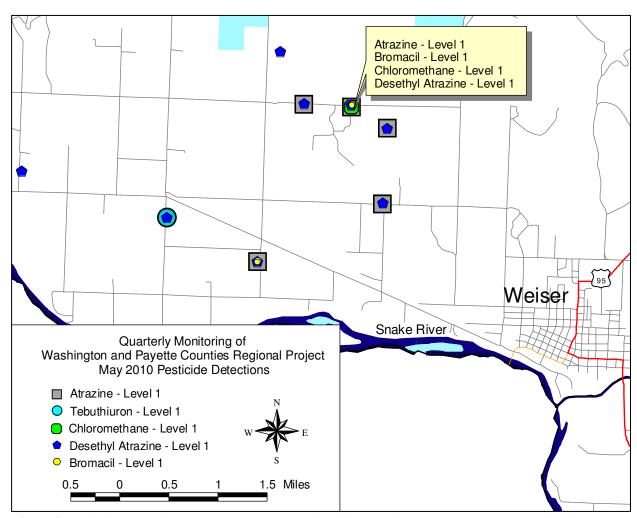
Five different pesticides and one Volatile Organic Compound (VOC) were detected in three wells sampled in Owyhee County, southwest of Homedale, during the

**Table 1.** 2009/2010 Quarterly Monitoring Discretionary Project Results from the November and February Sampling Events of Select Wells in the Washington and Payette Counties Regional Project.

Pesticide	Range (µg/L) (Min. – Max.)	Numl	Reference			
(Active Ingredient or Breakdown Product)		Novem- ber 2009	February 2010	May 2010	August <sup>1</sup> 2010	Point (µg/ L)
2,4-DCBA	0.09 (0.13 - 0.22)	0	3	0		91 (RfD) <sup>2</sup>
Atrazine	0.34 (0.03 - 0.37)	0	3	5		$3 (MCL)^3$
Bentazon	0.86	1	0	0	•••	200 (HAL)
Bromacil	0.71 (0.06 - 0.77)	3	3	2		90 (HAL)
Chloromethane	0.59	0	0	1	•••	30 (HAL)
DCPA (Dacthal)	0.04 (0.08 - 0.12)	1	1	0		70 (HAL)
Deisopropyl Atrazine	0.02(0.04 - 0.06)	2	1	0	•••	5
Desethyl Atrazine	1.97 (0.03 – 2)	5	5	8		5
Dinoseb	0.5	1	0	0		7 (MCL)
Metribuzin	0.5	1	0	0		200 (HAL)
Tebuthiuron	0.02 (0.06 - 0.08)	1	1	1	•••	500 (HAL)

<sup>&</sup>lt;sup>1</sup>Data is pending.

<sup>&</sup>lt;sup>5</sup> Breakdown product of Atrazine. No reference point available, MCL for Atrazine of 3 μg/L is used.



**Figure 2.** Pesticide results from ISDA May 2010 sampling of the Washington County wells west of Weiser, Idaho.

<sup>&</sup>lt;sup>2</sup>RfD – ISDA PMP Rule Calculated Reference Dose.

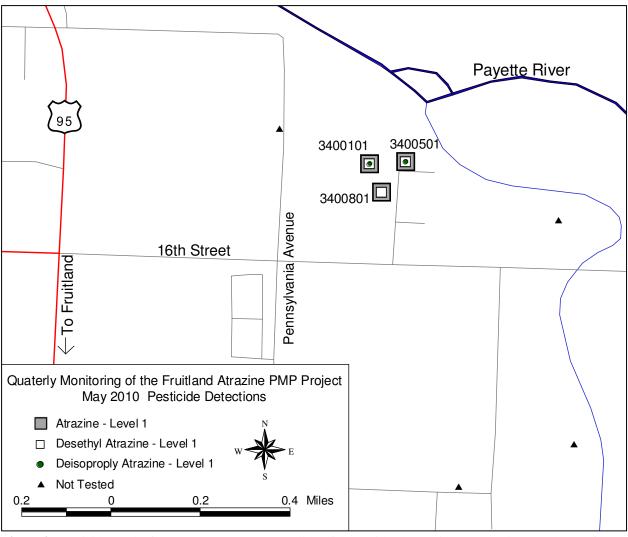
<sup>&</sup>lt;sup>3</sup> MCL – EPA Maximum Contaminant Level.

<sup>&</sup>lt;sup>4</sup> HAL – EPA Lifetime Health Advisory.

**Table 2.** 2009/2010 Quarterly Monitoring Discretionary Project Results from the November, February and May Sampling Events of Select Wells in the Fruitland Atrazine PMP Project.

Pesticide (Active Ingredient or	Range (µg/L) (Min. – Max.)	Sample Event with Detection (No. of Wells with Detection)				Reference Point (µg/
Breakdown Product)		Novem- ber 2009	Febru- ary 2010	May 2010	August <sup>1</sup> 2010	L)
2,4-DCBA	0.15	0	1	0		91 (RfD) <sup>2</sup>
Atrazine	0.1 (0.12 - 0.22)	3	3	3		$3 (MCL)^3$
Bromacil	0.09	1	0	0	•••	90 (HAL) <sup>4</sup>
Deisopropyl Atrazine	0.05 (0.03 – 0.08)	3	3	2	•••	5
Desethyl Atrazine	0.56 (0.2 - 0.76)	3	3	3		5

<sup>&</sup>lt;sup>1</sup>Data is pending.



**Figure 3.** Pesticide results from ISDA May 2010 sampling of the Fruitland Atrazine PMP Project, northeast of Fruitland, Idaho.

<sup>&</sup>lt;sup>2</sup>RfD – ISDA PMP Rule Calculated Reference Dose.

<sup>&</sup>lt;sup>3</sup>MCL – EPA Maximum Contaminant Level.

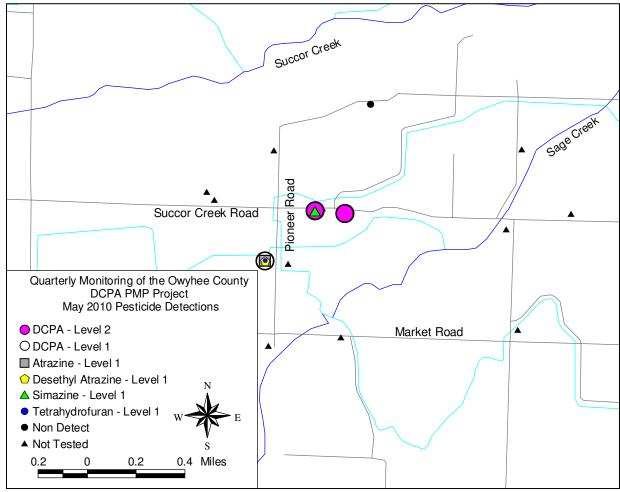
<sup>&</sup>lt;sup>4</sup>HAL – EPA Lifetime Health Advisory.

<sup>&</sup>lt;sup>5</sup>Breakdown product of Atrazine. No reference point available, MCL for Atrazine of 3 μg/L is used.

**Table 3.** 2009/2010 Quarterly Monitoring Discretionary Project Results from the November and February Sampling Events of Select Wells in the Owyhee County DCPA PMP Project.

Pesticide	Range (µg/L)	Numb	Reference			
(Active Ingredient or Breakdown Product)	(Min. – Max.)	November 2009	February 2010	May 2010	August <sup>1</sup> 2010	Point (µg/ L)
2,4-DCBA	0.07 (0.38 - 0.45)	0	2	0	•••	91 (RfD) <sup>2</sup>
Bromacil	0.06	1	0	0		90 (HAL) <sup>3</sup>
DCPA (Dacthal)	27.86 (0.14 – 28)	4	3	3	•••	70 (HAL)
Deisopropyl Atrazine	0.03	1	0	0		4
Desethyl Atrazine	0.01 (0.04 - 0.05)	0	1	1		4
Simazine	0.03	0	0	1	•••	$4 (MCL)^5$
Tetrahydrofuran	8.0	0	0	1	•••	50, 154 <sup>6</sup>

Data is pending.



**Figure 4.** 2009/2010 Discretionary Project quarterly monitoring results from Owyhee County DCPA PMP Project.

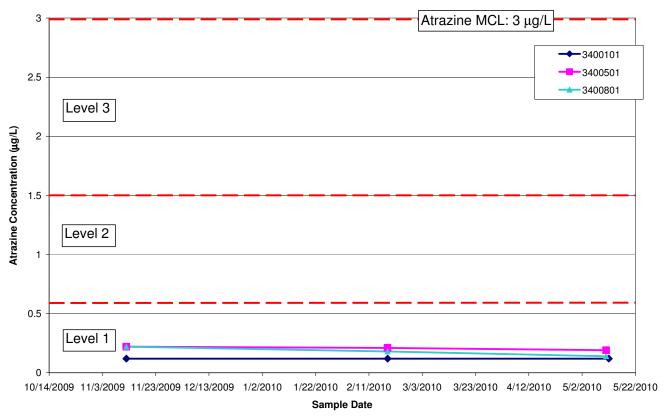
<sup>&</sup>lt;sup>2</sup>RfD – ISDA PMP Rule Calculated Reference Dose.

<sup>&</sup>lt;sup>3</sup>HAL – EPA Lifetime Health Advisory.

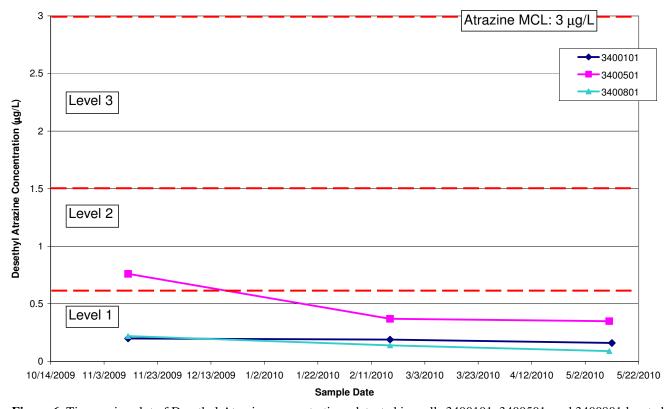
<sup>&</sup>lt;sup>4</sup>Breakdown product of Atrazine. No reference point available, MCL for Atrazine of 3 μg/L is used.

<sup>&</sup>lt;sup>5</sup>MCL – EPA Maximum Contaminant Level.

<sup>&</sup>lt;sup>6</sup>No EPA Standard exist, 50 μg/L is a Wisconsin Department of Natural Resources Drinking Water Guideline, 154 μg/L is a New Hampshire Department of Environmental Services Drinking Water Guideline

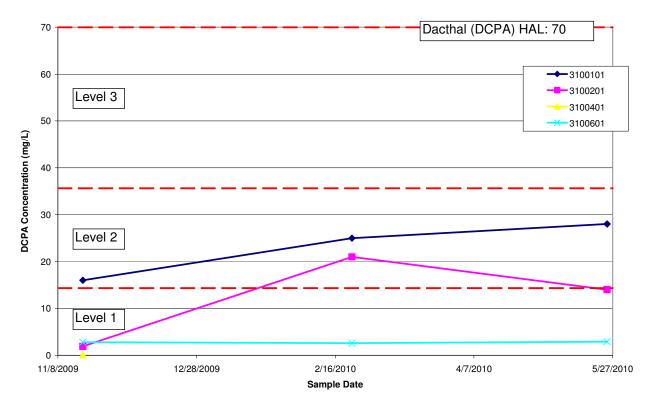


**Figure 5.** Time-series plot of Atrazine concentrations detected in wells 3400101, 3400501, and 3400801 located near Fruitland, Idaho.



**Figure 6.** Time-series plot of Desethyl Atrazine concentrations detected in wells 3400101, 3400501, and 3400801 located near Fruitland, Idaho.

#### **Discretionary Quarterly Monitoring - Owyhee County DCPA PMP Project**



**Figure 7.** Time-series plot of DCPA concentrations detected in three wells south of Homedale, Idaho in Owyhee County.

first three quarterly monitoring events (Table 3). The five pesticides detected in order of the number of detections include: DCPA (dacthal) (9), 2,4-DCBA (2), desethyl atrazine (2), atrazine (1), bromacil (1), deisopropyl atrazine (1), simazine (1), and tetrahydrofuran (1) (Table 3). Multiple detections in each well was common for all three quarters sampled. As established by the Idaho PMP Rule, there were Level 2 DCPA detections from the May 2010 in two of the three wells (Figure 4). One well had detections of DCPA, atrazine, desethyl atrazine, and tetrahydrofuran during the May 2010 sampling event. All detections were below any Idaho or EPA health standards (Table 3 and Figure 4). Time series plots through the quarterly period for DCPA (Figure 7) indicate that DCPA concentrations have increased to Level 2 values in wells 3100101 and 3100201.

#### Pesticide Descriptions

The following information summarizes the chemical characteristics and the labeled use of each pesticide that was detected in this project.

2,4-DCBA is a breakdown product of potentially several different pesticides including dicamba, propiconazole, dichlobenil, and dicofol. 2,4-DCBA is a hydrogenated

carboxylic acid and is slightly soluble in water.

Atrazine is a systemic triazine herbicide used to control broadleaf weeds and some grassy weeds (EPA, 2003). Laboratory studies have shown that atrazine is mobile and persistent and has had widespread detections in ground water and surface water (EPA, 2003). Atrazine is a restricted use pesticide and is registered for use in Idaho for corn, fallow grain fields, and non crop areas.

Desethyl Atrazine, or DEA, is a breakdown product of atrazine.

Deisopropyl Atrazine, or DIA, is a breakdown product of atrazine, simazine, and other triazines.

Chloromethane, is known as methyl chloride, is a colorless gas and is used as a soil fumigant in vegetable and fruit crops including onions.

DCPA, or dimethyl tetrachloroterephthalate, is a preemergent herbicide used to control annual grasses and broadleaf weeds. DCPA is commonly known by the trade name "Dacthal". DCPA is a general use product used on turf, ornamentals, strawberries, certain vegetables, onions, beans, and cotton. The two DCPA containing products currently registered in Idaho are Dacthal<sup>®</sup> Flowable Herbicide and Dacthal<sup>®</sup> W-75 Herbicide.

Bentazon is a general use post-emergence herbicide used for selective control of broadleaf weeds and sedges in beans, rice, corn, peanuts, mint, and others. Bentazon is a contact herbicide, which means that it causes injury only to the parts of the plant to which it is applied, interfering with the ability of susceptible plants to use sunlight for photosynthesis (Extoxnet, 2010). There are currently four products registered in Idaho with bentazon as an active ingredient.

Bromacil is a general use herbicide used for control of annual and perennial weeds (broadleaf and grasses), brush, and woody plants and vines in agricultural and non agricultural environments (EPA, 1996). Lab studies have shown that bromacil is very mobile in sand, sandy loam, clay loam, and silt loam soils (EPA, 1996). Bromacil is known to leach to the ground water as a result of normal use.

Dinoseb is a phenolic herbicide used in soybeans, vegetables, fruits and nuts, citrus, and other field crops (e.g., in corn) for the selective control of grass and broadleaf weeds. It is also used as an insecticide in grapes, and as a seed crop drying agent. It is produced in emulsifiable concentrates or as water soluble ammonium or amine salts. The use of dinoseb was cancelled in the U.S. in 1986. This action was based on the potential risk of birth defects and other adverse health effects for applicators and other persons with substantial dinoseb exposure (Extoxnet, 2010).

Metribuzin is a general use selective triazine herbicide which inhibits photosynthesis of susceptible plant species. Metribuzin is used for control of annual grasses and numerous broadleaf weeds in field and vegetable crops, in turfgrass, and on fallow lands (Extoxnet, 2010). Metribuzin is considered to be moderately persistence in the soil environment, with soil half-lives of 30 to 120 days, can be poorly bound to most soils and soluble in water, which allows for potential for leaching in many soil types (Extoxnet, 2010).

Simazine is a general use broad-spectrum triazine herbicide that is used to control broad-leaved weeds and annual grasses. Simazine is moderately persistent with an average field half-life of 60 days. Soil half-lives of 28-149 days have been reported (Extoxnet, 2010). Simazine has potential to leach to ground water depending on soil type, organic matter content, and agricultural practices.

Tebuthiuron is a general use broad-spectrum herbicide

used to control weeds in non-cropland areas, rangelands, rights-of-way, and industrial sites. It is effective on woody and herbaceous plants in grasslands. Tebuthiuron is highly persistent in soil. Reported field half-lives are from 12 to 15 months in areas with over 40 inches of annual rainfall, with longer half-lives expected in drier areas or in soils with high organic matter content (Extoxnet, 2010). Tebuthiuron is broken down slowly in the soil through microbial degradation. It is poorly bound to soil, suggesting high mobility. It was found in some ground water samples in Western states (Texas, California, Missouri, Oklahoma, and Washington) at levels up to  $3.8~\mu g/L$  (Extoxnet, 2010).

#### **Conclusions**

Results of testing indicate that pesticides have been found in all three alluvial aquifers tested as part of this project. The quarterly monitoring has been successful in identifying the existence of these pesticides and the associated trends. The majority of the wells sampled contained pesticide detections and even multiple detections. All detections were within health based levels. All detections were within Level 1 concentrations with the exception of DCPA detections south of Homedale, a November 2009 Level 3 desethyl atrazine detection west of Weiser, and the cumulative summation of the atrazine and atrazine breakdown products west of Weiser and near Fruitland in Payette County.

#### Recommendations

ISDA will respond to the pesticide detections from this project in accordance with the response section of IDAPA 02.03.01 Rules Governing Pesticide Management Plans For Ground Water Protection. ISDA will continue quarterly monitoring in 2010 and into 2011. ISDA may initiate additional quarterly monitoring for other areas in 2011.

ISDA personnel will continue to educate the pesticide applicators on the importance of adhering to label requirements and to apply all pesticides according to federal and state laws. ISDA personnel will continue to educate home and well owners in the area. ISDA staff will present the information to the PMP Advisory Committee, and implement the provisions of the Idaho PMP Rule.

# **Acknowledgments**

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